PATENT SPECIFICATION (11) 1454007

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(54) MARKING DEVICES

(71) We, OTTO SCHWANHAUSSER, GUNTER SCHWANHAUSSER AND HORST SCHWANHAUSSER trading as SCHWAN - BLEISTIFT - FABRIK SCHWANHAUSSER & CO., of D—8500 Nurnberg, Maxfeldstrasse 3, West Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

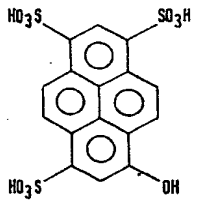
The invention relates to marking devices charged with marking solutions based on fluorescent dyestuffs.

Marking solutions which contain a dyestuff are used on a substantial scale in marking devices, especially those which possess a porous tip usually of fibre. In one example of the use of such solutions, written texts can be clearly highlighted, or optically contrasted with other texts, by painting-over with the solutions.

Marking solutions which contain a dyestuff which fluoresces in daylight, in organic solution, are known. These have the disadvantage that when used on paper they penetrate too deeply into the base. This reduces their fluorescent effect on the surface of the paper. However, it is also a shortcoming that the marking solutions strike through to the back of the paper, which may also carry writing.

Known marking solutions which contain a dyestuff which fluoresces in daylight in aqueous solution do not suffer from these shortcomings. However, when they are used, they show the disadvantage that, after application to a base and, evaporation of the solvent, the fluorescent effect only manifests itself at a relatively late stage, if at all. This reduces the utility of such marking solutions. One such marking solution which contains eosin in aqueous solution and suffers from this disadvantage is disclosed in British Specification No. 880,257.

According to the present invention, there is provided a marking device charged with a fluorescent aqueous marking solution comprising ions of hydroxypyrenetrisulphonic acid, *viz*, the compound of the formula:



and, optionally, further fluorescent or non-fluorescent dyestuffs in aqueous solution and which has a pH value in the alkaline range. Such a solution develops a strong fluorescence immediately after application to a base. This was not to be expected from experience with the known marking solutions which contain water-soluble dyestuffs which fluoresce in daylight, and all the less so since hydroxypyrenetrisulphonic acid in aqueous solution, after application to paper and drying, leaves no colouration detectable in normal light. The applied material can merely be rendered visible in ultraviolet light as a mark which fluoresces blue. If, however, in accordance with the present invention, hydroxypyrenetrisulphonic acid is used in aqueous alkaline solution, marks with a very strong fluorescent effect in the yellow region are obtained after application to paper, and the effect is also durable because of the alkalinity of the applied mark. To secure an intensely fluorescent effect, it is desirable to adjust the pH value of the marking solution to a value above 8.5 and generally below about 12. To ensure durable alkalinity in the applied mark, the alkalising agent (base) added to the marking solution should be preferably of low volatility.

The marking solution employed in the devices of the invention can be modified in various ways by the addition of further dyestuffs, for example to modify colour shade and fastness to light, and for these purposes both fluorescent and non-fluorescent dyestuffs can be used.

It is preferred to add to the marking solution in the marking devices, especially those with a porous stylus, a humectant, so that the solution does not dry up in the applicator tip.

An appropriate amount is 5 to 40% of the combined weight of the humectant and water. Glycols, such as diethylene glycol, can be employed for this purpose. The marking solution can also be used in other marking devices such as those having nibs or ball-points.

According to a further feature of the present invention, there is provided a method of marking a paper substrate which comprises applying to the substrate a fluorescent marking solution by a marking device as defined above and allowing the solution to dry.

Some examples of marking solutions according to the invention are given below:

EXAMPLE 1

Hydroxypyrenetrisulphonic acid (C.I. Solvent Green 7, No. 59,040)	1.5 g
Triethanolamine	10.0 g
Diglycol	20.0 g
Water	68.5 g

The pH value of the solution was about 11.3, and its colour was yellow.

EXAMPLE 2

Hydroxypyrenetrisulphonic acid	1.5 g
Sirius Light Turquoise Blue	0.4 g
Triethanolamine	10.0 g
Diglycol	20.0 g
Water	68.1 g

The pH value of the solution was about 11.2, and its colour was green.

EXAMPLE 3

Hydroxypyrenetrisulphonic acid	1.5 g
Sodium carbonate	1.5 g
Water	97.0 g

The pH value of the solution was about 10.5, and its colour was yellow.

WHAT WE CLAIM IS:—

1. A marking device charged with a fluorescent aqueous marking solution comprising hydroxypyrenetrisulphonic acid ions and having a pH value in the alkaline range.
2. A marking device according to claim 1, in which the solution has a pH value above 8.5 and below 12.
3. A marking device according to claim 1 or 2 wherein the pH value of the solution is adjusted by incorporating therein an alkalising agent of low volatility.
4. A marking device according to any one of the preceding claims, in which the solution also contains a humectant.
5. A marking device according to claim 4 in which the humectant is diethylene glycol.
6. A marking device according to claim 4 or 5 in which the solution contains 5 to 40% by weight of the humectant, based on the total weight of humectant and water.
7. A marking device according to any one of the preceding claims, in which the solution also contains a further fluorescent or non-fluorescent dyestuff.
8. A marking device according to any one of the preceding claims with a porous stylus.
9. A marking device according to claim 1 in which the solution is substantially as described in any one of Examples 1 to 3.
10. A method of marking a paper substrate which comprises applying to said substrate a fluorescent marking solution by a marking device as claimed in any one of the preceding claims and allowing the solution to dry.
11. Paper substrates marked by the method of claim 10.

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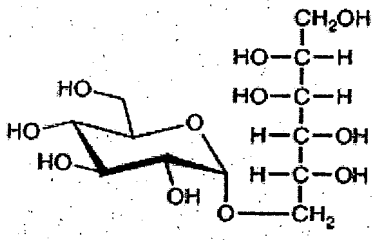
(4a)

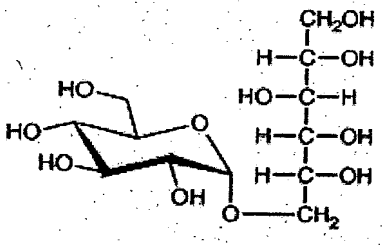
Palatinit®

Fachgebiet: Biotechnologie und Gentechnik, Unterthema: Lebensmittel, Ernährung, Enzyme
Siehe auch: Chemie, Lebensmittelchemie

(Isomalt, E 953). Äquimolare Mischung aus 6-*O*-α-D-Glucopyranosyl-D-sorbit (GPS) u. 1-*O*-α-D-Glucopyranosyl-D-mannit (GPM) [1] . Infolge des symmetr. Molekülaufbaues des Mannits sind im vorliegenden Falle die 1,6- u. 1,1-α-glucosid. Bindungen chem. gleich. GPM wird daher häufig auch als 6-*O*-α-D.... mannit bezeichnet.



GPM



GPS

Beide Zuckeralkohole entstehen durch katalyt. Hydrierung von *Palatinose®* (Isomaltulose), wobei durch Red. der Carbonyl-Gruppe des Fructose-Restes ein Diastereomerenpaar resultiert. Palatinose wird ihrerseits aus Saccharose mittels Transglucosidierung (s. Transglykosylierung) gebildet. Hierbei entsteht als Begleitsubstanz der Palatinose auch etwas *Trehalulose* (1-*O*-α-D-Glucopyranosyl-D-fructose). Letztere wird bei der katalyt. Hydrierung in 1-*O*-α-D-Glucopyranosyl-D-sorbit sowie -mannit überführt. Die Zuckeralkohole sind durch fraktionierte Krist. weitgehend trennbar. P. weist eine Süßkraft von 0,45 auf (bezogen auf Saccharose = 1, in 10%iger Lsg.). Von der Mundflora wie auch im Intestinaltrakt wird P. nur sehr langsam gespalten u. resorbiert. Sie ist somit weniger kariogen als Saccharose, wird vom Diabetiker besser toleriert u. nur zu 50% energet. genutzt (teilw. ausgeschieden) [2] . Bei Verabfolgung größerer Mengen wirkt P. laxierend.

Verwendung:

P. wird als Zuckeraustauschstoff für Diabetiker u. Übergewichtige sowie zur Herst. zahnschonender Süßigkeiten empfohlen. Applikationsgebiete: Süß-, Dauerback- u. Konditoreiwaren, Fruchtkonserven, Erfrischungsgetränke, Marmeladen, Konfitüren. Hersteller von P. ist Südzucker AG, Mannheim.

Übersetzungen:		CAS-RN:
E	palatinit	64519-82-0

Literatur:

[1] Lebensmittel- u. Biotechnol. **8**, 23–26 (1991).

[2] Rymon-Lipinski u. Schiweck, S. 338–344.

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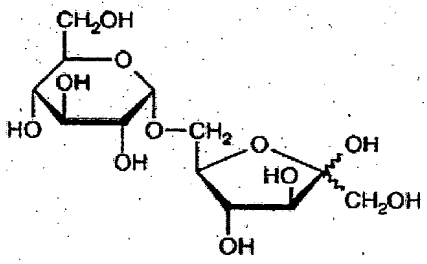
Ruttloff et al., S. 222ff.

(4b)

Palatinose®

Fachgebiet Biotechnologie und Gentechnik, Unterthema Lebensmittel, Ernährung, Enzyme
Fachgebiet Lebensmittelchemie, Unterthema Spezielle Lebensmittel (u.a. diätische Lebensmittel, Zuckeraustauschstoffe, Süßstoffe, Nahrungsergänzungsmittel)
Siehe auch: Naturstoffe

(Isomaltulose, 6-*O*-α-D-Glucopyranosyl-D-fructofuranose).



$C_{12}H_{22}O_{11}$, M_R 342,29, Schmp. 118–122°C, in Wasser leicht, in Alkohol wenig lösl.; $[\alpha]_D^{20}$ +97,2° (H_2O). Die süß schmeckenden Krist. sind in Wasser leicht, in Alkohol wenig löslich. Das Disaccharid P. besteht aus einer Glucose- u. einer Fructose-Einheit, die α-1,6-glykosid. verbunden sind. P. ist ein Struktur-Isomeres der Saccharose. P. ist krist. u. schmeckt angenehm süß. Die Süßkraft beträgt 0,4 (Saccharose = 1, in 10%iger Lsg.). Als Begleitprodukt ist vielfach in geringerer Menge *Trehalulose* (1-*O*-α-D-Glucopyranosyl-D-fructofuranose) anwesend.

Biochemie:

Im Intestinaltrakt wird P. langsamer als Saccharose in Glucose u. Fructose zerlegt u. demzufolge nur allmählich, z.T. nicht komplett resorbiert, so daß der Blutzuckerspiegel nach Verzehr weniger belastet wird (vorteilhaft für *Diabetiker*) [1] . Da P. von der Mundflora nicht gespalten werden kann, ist sie *weniger kariogen* als Saccharose [2] .

Vorkommen:

In Zuckerrohr-Extrakt u. Honig; sie wird von α-*Glucosyltransferase* (einer Transglykosylase) der Honigbiene aus Saccharose gebildet. Auch verschiedene Mikroorganismen synthetisieren dieses Enzym, so z.B. *Leuconostoc mesenteroides*, *Protaminobacter rubrum*, *Serratia phymutica*, *Erwinia rapontici*.

Herstellung [3] :

Eine 40%ige Saccharose-Lsg. wird nach Sterilisation kontinuierlich über einen Säulenreaktor mit trägerfixierten Zellen (Geleinschluß von *L. mesenteroides* od. *P. rubrum*) gegeben, welche die α-Glucosyltransferase produzieren. Dabei wird das Disaccharid zu 85% in P.

überführt. Neben P. können sich noch kleinere Anteile an Trehalulose, Isomaltose, Isomelicitose, Fructose od. Glucose vorfinden. Nach Entfärbung u. Entsalzung des Eluates wird dieses eingeengt, der Sirup zur Gewinnung von reiner, krist. P. wird angeimpft od. als solcher in den Handel gebracht [4] .

Verwendung:

Bislang nur in Japan zur Herst. von Süßwaren, Backwaren, Kaugummi u. ähnlichem. Ausgangsstoff für die Herst. des Disaccharid-Zuckeralkohols Palatinit®. Seine nur langsame bzw. nicht komplette intestinale Spaltung u. Resorption läßt P. auch für Diabetiker u. Übergewichtige interessant erscheinen; es ist in der BRD als Lebensmittelzusatzstoff nicht zugelassen.

Übersetzungen:	**CAS-RN:**
E palatinose®	13718-94-0

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[3] Proc. Res. Soc. Japan Sugar Refineries **33**, 55–63 (1984).

[4] Zuckerindustrie **116**, 197 (1991).

Beilstein EV **17/7**, 215

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